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(54) [Title of the Invention] Resin Composition for Calendering

(57) [Summary]

[Object] To provide a resin composition for calendering that possesses improved heat resistance, allows sheets to be formed by means of calendering, and comprises an amorphous polyester resin and polycarbonate resin.

[Means of Achievement] A resin composition comprising as its essential components montan acid wax and a mixed resin that contains 20 to 90 wt% of amorphous polyester resin and

80 to 10 wt% of polycarbonate resin, wherein the amorphous polyester resin of this resin composition is a copolymer in which, of the terephthalic acid component and ethylene glycol component thereof, part of the ethylene glycol component is substituted with 1,4-cyclohexanedimethanol.

[Claims]

[Claim 1] A resin composition for calendering, comprising as the essential components thereof montan acid wax and a mixed resin that contains 20 to 90 wt% of amorphous polyester resin and 80 to 10 wt% of polycarbonate resin of a fatty acid ester, wherein the amorphous polyester resin of the resin composition is a copolymer in which, of the terephthalic acid component and ethylene glycol component thereof, part of the ethylene glycol component is substituted with 1,4-cyclohexanedimethanol.

[Claim 2] The resin composition for calendering according to claim 1, wherein the average molecular weight of the polycarbonate resin in the mixed resin is 10,000 to 25,000.

[Claim 3] The resin composition for calendering according to claim 1 or claim 2, wherein the mixture ratio of the mixed resin and the montan acid wax based on a fatty acid ester is 0.1 to 5.0 parts by weight of the montan acid wax per 100 parts by weight of this mixed resin.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a resin composition for calendering with which sheets comprising a polyester resin with improved heat resistance can be molded.

[0002]

[Prior Art] In general, polyester resins such as polyethylene terephthalate (PET) have been widely used for years in fibers, films, and the like.

[0003] Of these, the commonly used films are transparent films that have little temperature dependency in the normally used temperature environments and that possess excellent tensile strength, impact strength, tear strength, and other mechanical properties, as well as excellent chemical resistance, solvent resistance, and electrical insulation performance. These films are obtained by means of processes in which the above-mentioned resin is extruded in a molten state

by extrusion molding, the molten resin is quenched and solidified, the solidified resin is biaxially drawn and crystallized, and the crystallized resin is then heated and set at a specific temperature.

[0004] As stated above, this type of film is obtained using a crystalline resin as the starting material; therefore, biaxial drawing or another drawing means is necessary in order to obtain a product having good mechanical properties and transparency. As a result, laminar objects with a thickness of 0.3 mm or more, which are normally referred to as "sheets," cannot be obtained.

[0005] Moreover, even if a sheet is obtained from the above-mentioned resin, the resin component is a crystalline resin; therefore, the resin has low viscosity when heated, so-called secondary thermoforming by means of vacuum molding or compression molding cannot be performed, and adhesion with organic solvents or the like is difficult to achieve.

[0006]

[Problems to Be Solved by the Invention] Means for improving the properties of the above-mentioned polyester resins themselves have been devised in recent years, and the improved resins are being widely used in order to improve extrusion moldability and to obtain sheets from this resin while keeping its original mechanical properties and transparency within a range that is acceptable for practical use. Specifically, so called amorphous polyethylene terephthalate, which is obtained by means of substituting part of the ethylene glycol with cyclohexanediol when dimethyl terephthalate and ethylene glycol are polycondensed by means of transesterification, is used as the starting material for extrusion molding to obtain a sheet.

[0007] However, this amorphous polyethylene terephthalate has poor heat resistance. To overcome this shortcoming, a method is used whereby another thermoplastic resin that is compatible with this amorphous polyethylene terephthalate and has better heat resistance than this amorphous polyethylene terephthalate is added, and a sheet is obtained by means of extrusion molding.

[0008] Nevertheless, it is a known technical fact that the amount of sheet produced (amount extruded) per unit of time by means of conventional extrusion molding methods is much smaller than by means of calendering because of constraints in terms of equipment structure.

[0009] Therefore, the use of the above-mentioned amorphous polyethylene terephthalate for calendering was considered in order to improve productivity, but using this resin alone is impossible in practical terms for the following reason. That is, this resin has low viscosity when thermoformed, and it firmly adheres to the metal roll surface of the calendering machine, will not

peel off, and hence cannot be molded into a laminar object. This problem also occurs in methods of adding a thermoplastic resin with strong heat resistance or the like in order to improve the heat resistance of the amorphous polyethylene terephthalate.

[0010] The inventors completed the present invention upon discovering that in order to mold a mixed resin, obtained by means of mixing the above-mentioned amorphous polyethylene terephthalate as the polyester resin and a resin that is compatible with this amorphous polyethylene terephthalate and has better heat resistance than this amorphous polyethylene terephthalate, into sheets by means of thermomolding using the calendering method, a specific lubricant should be selected and added to the above-mentioned resin components, and the resulting resin composition should be used as the starting material.

[0011] That is, an object of this invention is to provide a resin composition for calendering comprising an amorphous polyester resin and a polycarbonate resin with which it is possible to mold sheets by means of calendering.

[0012]

[Means Used to Solve the Above-Mentioned Problems] Aimed at attaining the stated object, the present invention resides in a resin composition for calendering comprising as its essential components montan acid wax and a mixed resin that contains 20 to 90 wt% of amorphous polyester resin and 80 to 10 wt% of polycarbonate resin of a fatty acid ester, wherein the amorphous polyester resin of this resin composition is a copolymer in which, of the terephthalic acid component and the ethylene glycol component, part of the ethylene glycol component is substituted with 1,4-cyclohexanedimethanol.

[0013] A preferred embodiment of the present invention involves the resin composition for calendering according to claim 1 wherein the average molecular weight of the polycarbonate resin of the mixed resin is 10,000 to 25,000, as described in claim 2.

[0014] Another preferred embodiment of the present invention involves the resin composition for calendering according to claim 1 or 2 wherein the mixture ratio of the mixed resin and the montan acid wax based on a fatty acid ester is 0.1 to 5.0 parts by weight of this montan acid per 100 parts by weight of this mixed resin, as described in claim 3.

[0015] The amorphous polyester resin, which is part of the mixed resin and is an essential component of the resin composition for calendering of the present invention, is in a ratio at which the amount of 1,4-cyclohexanedimethanol is 10 to 90 mol% in relation to 90 to 10 mol%

of ethylene glycol. In this case, when the ethylene glycol and 1,4-cyclohexanedimethanol are outside the above-mentioned range, crystallinity of the amorphous polyester resin increases and calendering becomes difficult. Therefore, the preferred range is 20 to 60 mol% of 1,4-cyclohexanedimethanol in relation to 80 to 40 mol% of ethylene glycol component.

[0016] In addition, if the average molecular weight of the polycarbonate resin, which is part of the mixed resin and is an essential component of the resin composition for calendering, exceeds 25,000, the melting temperature of this polycarbonate resin will rise, the temperature when it melts together with the polyester resin will increase, there will be a reduction in viscosity of the entire resin composition, and molding of sheets with a calendering machine will be impossible. Moreover, an average molecular weight of less than 10,000 is not suitable because there will be a reduction in heat resistance of the resin composition itself, as well as a deterioration of impact resistance. Consequently, the average molecular weight is preferably within a range of 15,000 to 20,000.

[0017] If the mixture ratio of amorphous polyester resin and polycarbonate resin in the mixed resin exceeds 80 wt% of polycarbonate resin in terms of amorphous polyester resin, the working temperature will rise, the material will be difficult to work, and calendering performance of the molten resin will be so poor that a sheet will not be made. In addition, if there is less than 10 wt% of polycarbonate resin, heat resistance will be inferior. Consequently, it is preferred that the ratio be 40 to 70 wt% of amorphous polyester resin and 60 to 30 wt% of polycarbonate resin.

[0018] Next, the lubricant that is used with the mixed resin in the present invention is an ester compound of montan acid and an alcohol. The montan acid wax based on a fatty acid ester is used. The alcohol in this case is ethylene glycol, 1,2-butanediol, 1,3-butanediol, 2,3-butanediol, glycerol, or the like. Moreover, the montan acid wax can be partially saponified.

[0019] The amount in which this montan acid wax is added is 0.1 to 5.0 parts by weight of montan acid wax per 100 parts by weight of the mixed resin.

[0020] In this case, there will be extreme adhesion of this resin composition for calendering to the metal roll surface of the calendering machine if the amount in which the montan acid wax is added is less than 0.1 part by weight, and it will not be possible to peel this resin in sheet form from the metal roll. Therefore, the preferred amount of montan acid wax is 0.5 to 5.0 parts by weight. In addition, if the amount exceeds 5 parts by weight, the extent to which this resin composition for calendering adheres to the metal roll surface will be diminished, and there will

be a reduction in viscosity when molten and the resin separate in sheet form from the metal roll surface. However, excess elongation will be produced by means of the weight of the sheet itself, and it will not be possible to mold the material into sheet form. Therefore, the preferred amount of this montan acid wax is 0.1 to 4 parts by weight.

[0021] Furthermore, in addition to the montan acid wax and the mixed resin comprising an amorphous polyester resin and a polycarbonate resin, which are the above-mentioned essential components, it is possible to add other lubricants as components of the resin composition for calendering of the present invention. These lubricants serve as auxiliary agents designed to aid in releasing the resin from the metal rolls of the calendering machine. For instance, hydrocarbon lubricants such as paraffin wax, fatty acid lubricants such as stearic acid, and fatty acid amide lubricants such as stearylamide, as well as fatty acid esters, alcohols, metallic soaps, and other various lubricants may be used jointly.

[0022] Moreover, phenols, hindered amines, phosphorus stabilizers, various types of fillers, various pigments, and the like can be added as other additives within a range that will not compromise the purpose of the present invention.

[0023]

[Working Examples] Working examples that show embodiments of the resin composition for calendering of the present invention will now be described together with comparative examples.

[0024] <u>Working Examples 1 through 8</u>

The amorphous polyester resin portion of the mixed resin was a copolymer in which, of the terephthalic acid component and ethylene glycol component that formed the resin portion, part of the ethylene glycol component was substituted with 1,4-cyclohexanedimethanol, and the ratio of the components was 65 mol% of 1,4-cxyclohexanedimethanol per 35 mol% of ethylene glycol.

[0025] Moreover, three types of polycarbonate with average molecular weights of 12,000, 16,000, and 23,000 were used as the polycarbonate resin portion of the mixed resin.

[0026] Montan acid wax, which is an ester compound of montan acid and alcohol, with the alcohol being 1,3-butanediol, was used as the essential lubricant component.

[0027] Next, the amorphous polyester resin, polycarbonate resin, and montan acid wax were mixed at the ratios shown in Table 1 for each working example, pre-heated, and kneaded by means of a biaxial extruder as a pre-treatment. The material was then transferred to an L-shaped

calendering machine comprising four metal rolls with a roll diameter of 250 mm, and calendered under conditions corresponding to a roll temperature of 170 to 180°C in order to mold sheets with a thickness of 0.5 mm.

[0028] The numbers in Table 1 show the mixture ratio (as percent by weight) of amorphous polyester resin and polycarbonate resin in the mixed resin, and the ratio of montan acid wax (as parts by weight) per 100 parts by weight of this mixed resin. The amorphous polyester resin is indicated as "amorphous PET," and the polycarbonate resins are indicated as "PC-1 through PC-3" and are classified by average molecular weight. The numbers in brackets are the average molecular weights.

[0029]

[Table 1]

		Comparative examples							
		1	2	3	4	5	6	7	8
Resin composition	Amorphous PET	70	70	70	40	50	60	70	70
	PC-1 [12,000]	30			60				
	PC-2 [16,000]		30			50		30	30
	PC-3 [23,000]			30			40		
	Montan acid wax	4.0	4.0	4.0	2.0	2.0	2.0	0.5	4.0
Evaluation	Moldability	O	O	O	O	O	O	O	O
	Heat resistance	O	O	O	O	O	O	O	O

[0030] The results of evaluating moldability during the above-mentioned molding of sheets on a calendering machine and of evaluating the heat resistance of the resulting sheets were good moldability (represented by O) when molding of sheets was possible, and poor moldability (represented by ×) when molding of sheets was impossible, as well as good heat resistance (represented by O) when the thermal deformation temperature was determined to exceed 80°C, and poor heat resistance (represented by ×) when the thermal deformation temperature was determined to be 80°C or lower. These are both shown in Table 1 for each working example.

[0031] By means of above-mentioned Working Examples 1 through 8, it was possible to obtain without difficulty sheets that had the desired thickness of 0.5 mm and possessed such good release performance that there was only slight adhesion of any of the resin compositions to the

metal rolls of the calendering machine, and, as shown in Table 1, moldability by means of calendering was adequate, and heat resistance was high with each of the resin compositions.

[0032] Comparative Examples 1 through 6

The same amorphous polyester (amorphous PET) as the one used in the working examples was used for the polyester resin, as was a crystalline polyester resin in which the ethylene component was not substituted by 1,4-cyclohexanedimethanol or another component, that is, polyethylene terephthalate "PET" (as opposed to the "amorphous PET" of the working examples). Also, "PC-4," a resin with an average molecular weight of 19,000, and "PC-5," a resin with an average molecular weight of 27,000, were used as the polycarbonate resins, as indicated by the components and mixture ratios shown in Table 2, in contrast to the working examples. Moreover, with the exception of Comparative Example 2, the same montan acid wax as in the working examples was used as the lubricant in all of the comparative examples. Other than the fact that the mixture ratio of "PET" and polycarbonate resin in Comparative Examples 5 and 6 is indicated as percent by weight, and the mixture ratio of montan acid wax is indicated as parts by weight per 100 parts by weight of "PET," the quantities in the comparative examples are in the same units as in the working examples.

[0033] Next, the above-mentioned resins and lubricants were mixed at the mixture ratios shown in Table 2, and the resulting mixtures were used in an attempt to mold sheets of the same thickness and by means of the same procedure as in the working examples. The results of evaluations, which were conducted in the same manner as in the working examples, are listed in Table 2.

[0034]

[Table 2]

		Comparative examples					
		1	2	3	4	5	6
Resin composition	Amorphous PET	70	70	5	95		
	PET					70	70
	PC-4 [19,000]		30	95	5	30	
	PC-5 [27,000]	30					30
	Montan acid wax	2.0	–	1.0	3.0	4.5	4.5
Evaluation	Moldability	×	×	×	O	×	×
	Heat resistance	–	–	–	×	–	–

[0035] In the case of Comparative Examples 1 through 3, a high temperature was necessary because the mixture gelled after it was transferred from the extruder to the calendering machine. Moreover, melt viscosity decreased considerably and the mixture adhered and could not be released from the metal roll of the calendering machine, making it impossible to obtain a sheet.

[0036] In addition, in Comparative Example 4, the resin gelled at an extruder cylinder temperature of 180°C and could be transferred to the calendering machine. It did not adhere firmly to the metal roll and was smoothly released, making it possible to mold sheets. However, heat resistance was poor, with the thermal deformation temperature of the resulting sheets being 72°C.

[0037] Furthermore, molding of sheets was impossible in Comparative Examples 5 and 6 because the mixture would not gel.

[0038]

[Results of the Invention] As previously explained, the resin composition for calendering of the present invention comprises as its essential components montan acid wax based on a fatty acid ester, and a mixed resin comprising 20 to 90 wt% of amorphous polyester resin and 80 to 10 wt% of polycarbonate resin, wherein the amorphous polyester resin of this resin composition is a copolymer in which, of the terephthalic acid component and the ethylene glycol component, part of the ethylene glycol component is substituted with 1,4-cyclohexanedimethanol. The resulting merit is that viscosity during heating is appropriately high and adhesion to the metal roll surface of the calendering machine is diminished so that the resin can be easily released, making is possible to mold sheets by means of calendering, to improve considerably the amount of sheets produced per unit time, and to enhance the heat resistance of the resulting sheets.

[0039] In addition, the resin composition for calendering of the present invention is the resin composition according to claim 1 wherein the average molecular weight of the polycarbonate resin in this mixed resin is 10,000 to 25,000, with the resulting advantage being that the original mechanical properties and transparency of polyester can be kept within a range that is acceptable for practical use while adjusting as needed the melt viscosity and adhesion to the metal roll and establishing calendering conditions that are optimum for calendering, as described in claim 2.

[0040] Furthermore, the resin composition for calendering of the present invention is the resin composition according to claim 1 or claim 2 wherein the mixture ratio of this mixed resin and the

montan wax of a fatty acid ester is 0.1 to 5.0 parts by weight per 100 parts by weight of this mixed resin, with the resulting advantage being that it is not necessary to raise excessively the molding temperature during calendering and that a sheet with improved heat resistance can be obtained, as described in claim 3.

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